PTZ™ PHENOTHIAZINE

A Stabilizer For A Variety Of Chemical Applications

INTRODUCTION

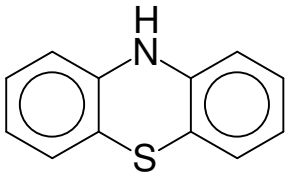
PTZ Phenothiazine is an aromatic amine based product that exhibits broad activity as an inhibitor, antioxidant and shortstopping agent in a variety of diverse applications. The product is principally utilized as an inhibitor and shortstopping agent in the stabilization of acrylic acids, esters and monomers. Other inhibitor and shortstopping applications include the stabilization of chloroprene monomer/neoprene polymer, styrene monomer and other vinylic monomers. The product is used as an antioxidant in synthetic lubricants and oils, polyols for polyurethanes and polyester and vinyl ester resins. PTZ Phenothiazine also finds application as a pharmaceutical intermediate.

In its many applications, PTZ Phenothiazine avails the customer a variety of benefits. The product is extremely active, functions at very low concentrations and will synergize with other stabilizers. The product will function in strongly acidic environments and is one of the few inhibitors that perform in either air or nitrogen environments. Chemical processes in which the product is utilized, as a monomer stabilizer will exhibit improved onstream factor, greater operational flexibility and increased production output. Products and chemical processes that utilize PTZ Phenothiazine will exhibit enhanced and improved performance.

PHYSICAL AND CHEMICAL PROPERTIES

A. Structure and Characteristics

PTZ Phenothiazine is a solid product that is supplied in both flake and powder forms. The chemical structure, nomenclature, general characteristics and properties of the product are as follows:



PTZ Phenothiazine

Chemical Name:	Thiodiphenylamine
Empirical Formula:	$C_{12}H_9NS$
Molecular Weight:	199.26
Appearance:	Yellow flakes or powder
Melting Point, °C	184
Boiling Point, °C	371
TGA (10% wt. Loss), °C	216
Bulk Density	0.85 (flake) and 0.75 (powder)

B. Product Specifications

PTZ Phenothiazine is sold in both flake and powder forms to the specifications detailed in the following table.

PTZ Phenothiazine Product Specifications		
Specification	Flake	Powder
Appearance	Yellow flakes	Yellow powder
Purity, wt. % min.	99.6	99.6
Melting Point, °C, min.	184	184
Particle Size, microns	>500 (94% min.)	<700 (98% min)

C. Solubility

The solubility of PTZ Phenothiazine in a variety of common solvents and other organic chemicals is as detailed in the table below:

PTZ Phenothiazine Solubilities

Solvent	gms phenothiazine/100 gms solvent
Acetone	20
Acetophenone	19
Ethyl Acetate	10
Methyl Methacrylate	6.5
Ethyl Acrylate	6
Butyl Acrylate	6
Styrene Monomer	2.5
Ethylbenzene	1.5
Acrylic Acid	1.5
Methacrylic Acid	1.5
Ethanol	1.0
Water	Nil

D. Vapor Pressure

The table below details the vapor pressure of PTZ Phenothiazine over a range of temperatures.

PTZ Phenothiazine Vapor Pressure	
Temperature (°C)	Vapor Pressure (mm Hg)
371	760
290	130
130	1

FEATURES AND BENEFITS

- Broad stabilizer activity allows the product to function as either an inhibitor, antioxidant or shortstopping agent in a range of diverse applications
- Outstanding thermal stability facilitates performance at temperatures of 90 °C and above
- Acid resistant, will perform in low pH environments
- Operational versatility, functions in both aerobic and anaerobic environments
- High activity leads to functionality at low concentrations
- Synergizes with other stabilizer products allowing the formulation of high efficiency systems
- Low cost, economical product

TECHNOLOGY DISCUSSION

PTZ Phenothiazine is a free radical inhibitor that functions via an abstraction mechanism. This is true of the product whether it is utilized as either a vinyl monomer inhibitor or as an antioxidant in the stabilization of products prone to undergo oxidative degradation. The section below discusses the usage of PTZ Phenothiazine and other inhibitors in the stabilization of vinyl monomers to prevent their polymerization during manufacture, distillation and storage. The mechanism discussed in this section would also be applicable to the usage of the product as an antioxidant.

Mechanism of Inhibition in Vinyl Monomers

Typical stabilizers utilized in the stabilization of vinyl monomers include PTZ Phenothiazine, hydroquinone, and the monomethyl ether of hydroquinone, phenolics and amines. All of these products function via either an abstraction or radical addition mechanism. In some vinyl monomer applications it is common practice to utilize these products in combination with each other to achieve synergistic and enhanced performance.

During production and storage, monomers may undergo free radical polymerization. This rapid polymerization is the result of monomer species achieving a free radical state that leads to further reaction and polymer formation. This free radical state is achieved through the monomer interacting with oxygen, an oxygen complex, an impurity or the reactor wall. The function of the inhibitor is to scavenge the initiating radical or terminate the growing polymer chain. To be effective, an inhibitor must interact with the radical species to produce an intermediate that is less reactive.

Equation 1 illustrates how a radical (R•) interacts with a monomer species to produce an unstable radical monomer species that is prone to further polymerization. Equations 2 and 3 illustrate two methods by which an inhibitor (IH) may terminate the radical species that is responsible for the generation of the radical monomer.

$$R\bullet + CH_2{=}CHCOOH \rightarrow R\text{-}CH_2\text{-}\underset{\bullet}{C}HCOOH \qquad (1)$$

$$R\bullet + IH \rightarrow RH + I\bullet \qquad (2)$$

$$R\bullet + IH \rightarrow RIH\bullet \qquad (3)$$

Equation 2 would be typical of an abstraction mechanism and would be common to phenolic and amine type inhibitors. Equation 3 would be typical of an addition reaction, common to quinone inhibitors.

If allowed to continue to react unchecked, the monomer radical generated in Equation 1 would continue to react with other monomers and form a growing polymer chain. Equation 4 illustrates a hydrogen atom transfer from a polymer radical (P•) to the inhibitor, producing a terminal double bond on the polymer chain and a new less reactive free radical.

$$P\text{-}\underset{\bullet}{C}H_2\text{-}CHCOOH + IH \rightarrow P\text{-}CH{=}CHCOOH + IH_2 \qquad (4)$$

Alternatively, the polymer radical may extract a hydrogen atom from the inhibitor molecule, leading to the formation of a stable polymer and a less reactive radical.

$$P\text{-}\underset{\bullet}{C}H_2\text{-}CHCOOH + IH \rightarrow P\text{-}CH_2\text{-}CH_2COOH + I\bullet \qquad (5)$$

Another possible method for terminating the reaction is an addition mechanism as is shown in reaction 6.

$$P\text{-}\underset{\bullet}{C}H_2\text{-}CHCOOH + IH \rightarrow P\text{-}CH_2\text{-}\underset{\vert}{\underset{IH\bullet}{C}}HCOOH \qquad (6)$$

In equations, 4 through 6, the radical reacts with an inhibitor molecule to produce a less reactive radical.

Radicals are removed from the system through disproportionation and combination reactions as detailed in equations 7 and 8. In equations 7 and 8 both reactants are radicals but they might not necessarily be the same species.

$$R_1H\bullet + R_2H\bullet \rightarrow R_1 + R_2H_2 \qquad (7)$$

$$R_1\bullet + R_2\bullet \rightarrow R_1\,R_2 \qquad (8)$$

PTZ PHENOTHIAZINE - APPLICATIONS

When utilized as either a monomer inhibitor, antioxidant or shortstopping agent, PTZ Phenothiazine imparts outstanding stability to the final product.

As a monomer stabilizer, PTZ Phenothiazine increases the inherent stability of the monomer, protecting it from uncontrolled polymerization, which can lead to equipment fouling or pluggage and downtime. As a result of improvements achieved in monomer stability, operational flexibility and performance are improved and production output increased. Additionally, since polymer formation is minimized, plant residues, waste and disposal costs will be reduced.

Acrylic, styrenic and other vinylic monomers represent the general classes of products in which PTZ Phenothiazine finds application. Specific examples of the monomers are as follows:

- Acrylic acids, esters and monomers (i.e. AA, BA, EA, 2EHA, MMA, MAA, etc).
- Chloroprene monomer/neoprene polymer
- Specialty acrylic esters
- Vinyl pyridine monomer
- Styrene monomer

These monomers find usage in a variety of diverse applications, such as superabsorbent polymers, coatings, adhesives, acrylic polymers, plastics and rubbers. In the production, transportation and final conversion of these monomers, it is critical that they be properly protected from premature polymerization. PTZ Phenothiazine is an outstanding in process, storage and transportation stabilizer for these types of monomers.

As an antioxidant, PTZ Phenothiazine protects products from undergoing oxidative degradation and the resultant changes in product aesthetics, physical properties and performance in end use applications. Product lifetimes are increased through the usage of PTZ phenothiazine in these applications. Examples of the areas in which PTZ Phenothiazine finds usage as an antioxidant include:

- Lubricants and oils (i.e. synthetic, epoxy, heat transfer and functional fluids)
- Polyols for polyurethanes
- Unsaturated polyesters and vinyl resins

Cytec Industries Inc. has conducted extensive testing of PTZ Phenothiazine in a variety of these applications. In these tests, PTZ Phenothiazine was determined to increase the stability of the various monomers and other products. Evaluations were conducted via industry specific test protocols and recommendations.

A. Acrylic Acids, Esters and Monomers

During production and storage, acrylic acids, esters and monomers may undergo free radical polymerization. This polymerization leads to polymer formation, which can cause product build-up and plugging of distillation columns. In extreme cases, polymerization can occur very rapidly and lead to pluggage of lines or more catastrophic events, like fires and explosions.

PTZ Phenothiazine is widely utilized as a monomer stabilizer in the production of acrylic acids, esters and monomers. In this industry the product is principally utilized as either an "in process" monomer stabilizer or as a monomer storage and transportation stabilizer.

In acrylic acid, ester and monomer applications, the product performs the following functions:

- Prevents polymerization of acids and monomers during their manufacture
- Protects acids during their esterification to esters and subsequent distillation/purification
- Protects crude acids and monomers during storage and transportation (i.e. shipment)
- Functions as a shortstopping agent for runaway polymerizations

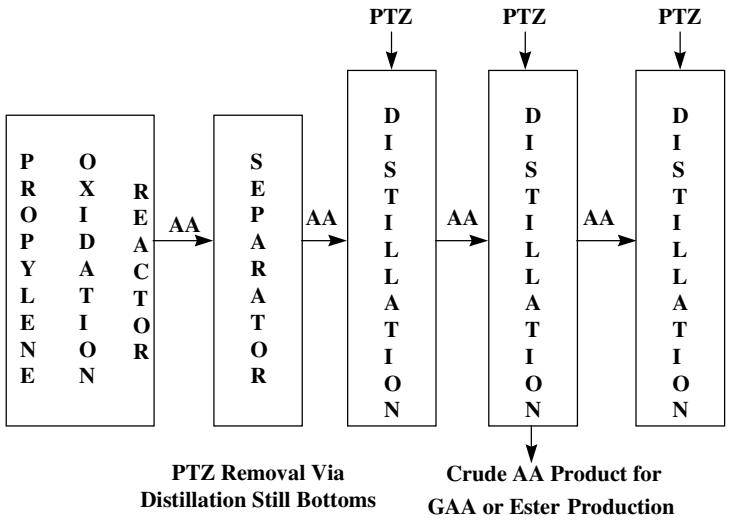
Dependent upon the manufacturing process, PTZ Phenothiazine may be used either alone or in combination with other types of inhibitors such as hydroquinone, carbamates, nitroxyl or other stabilizer products. Process diagrams 1, 2 and 3 illustrate simplified, typical processes for producing acrylic acids, esters and monomers and show methods of product addition and removal.

1. Incorporation and Removal of PTZ Phenothiazine

Typically, PTZ Phenothiazine is incorporated into the acrylic acid, ester or monomer manufacturing process via solubilization in a suitable process solvent. This type of addition assures that the PTZ Phenothiazine stabilizer will become intimately dispersed and impart adequate protection to the acid or monomer. Dependent upon the production technology, the product may be incorporated at various stages during the production and distillation of the acid and monomer products. Usually, PTZ Phenothiazine is removed from the process in the distillation still bottoms.

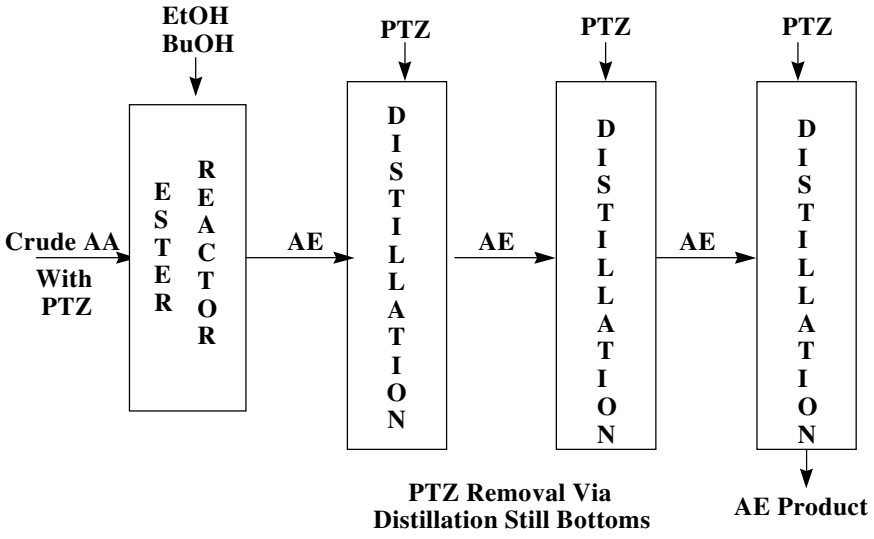
Process Diagram 1

PTZ Phenothiazine - In Process Stabilization of Acrylic Acid



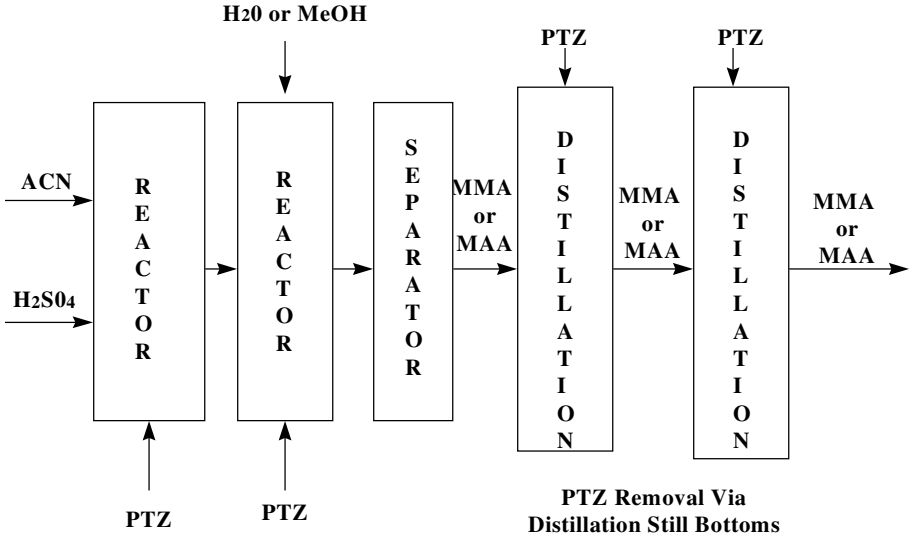
Process Diagram 2

PTZ Phenothiazine - In Process Stabilization of Acrylic Esters



Process Diagram 3

PTZ Phenothiazine in MAA and MMA Production



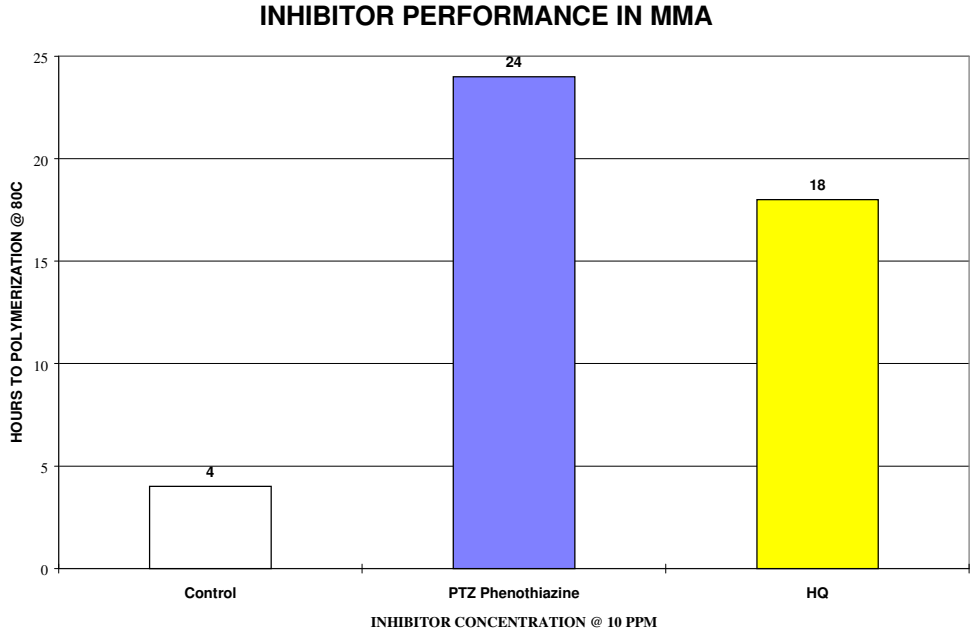
2. PTZ Phenothiazine Performance in Acrylic Acids, Esters and Monomers

The following information represents the results of evaluations conducted in our laboratory on the performance of PTZ Phenothiazine in the stabilization of acrylic acids, esters and monomers. In these evaluations, the effectiveness of PTZ Phenothiazine was assessed by measuring the time to onset of polymerization of the monomer solution. Initially, the monomers were washed and stripped of the base inhibitor and then the inhibitors were reincorporated to the noted concentrations. The monomers were then placed in an oil bath at an elevated temperature and the time to the onset of polymerization measured. The onset of polymerization was determined via either thermocouple monitoring of the monomer for an exothermic temperature rise indicative of the onset of polymerization, or visual examination for polymer formation.

PTZ Phenothiazine Performance in MMA

Graph 1 details the performance of PTZ Phenothiazine in Methyl Methacrylate (MMA).

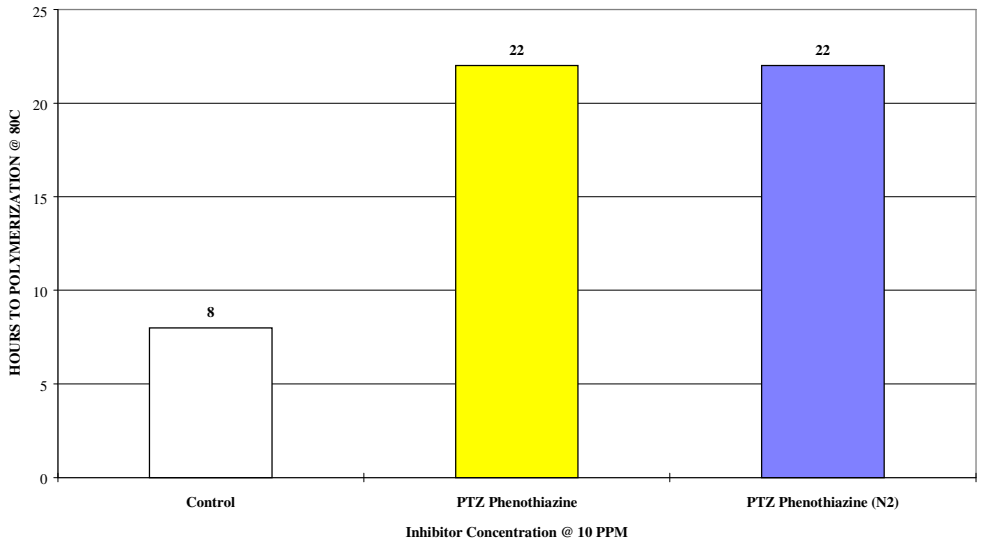
Graph 1



Graph 2 demonstrates the performance of PTZ Phenothiazine in MMA in both air and environments. PTZ Phenothiazine is one of few stabilizers able to function in both aerobic and anaerobic environments.

Graph 2

INHIBITOR PERFORMANCE IN MMA - AIR AND NITROGEN

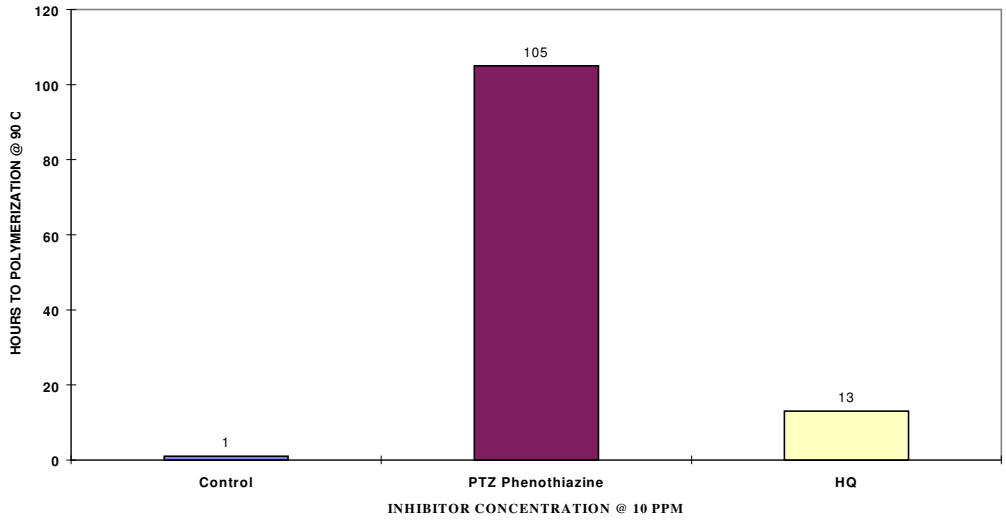


PTZ Phenothiazine Performance in Butyl Acrylate

Graph 3 shows the performance of PTZ Phenothiazine in Butyl Acrylate (BA)

Graph 3

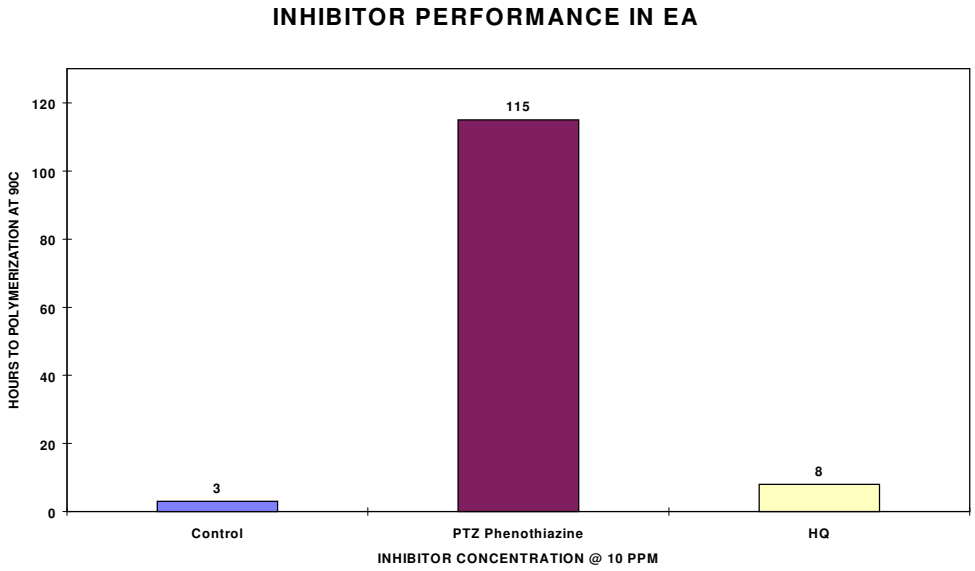
INHIBITOR PERFORMANCE IN BA



PTZ Performance in Ethyl Acrylate (EA)

Graph 4 illustrates the performance of PTZ Phenothiazine in Ethyl Acrylate.

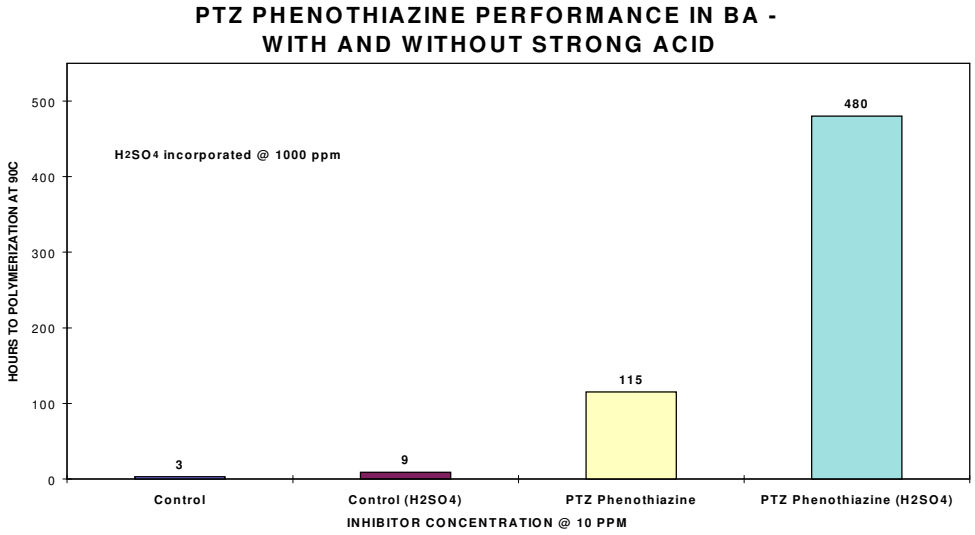
Graph 4



PTZ Performance in Acidic Environments

One of the unique characteristics of PTZ Phenothiazine is its ability to function in strongly acidic environments. Graph 5 details the performance of PTZ Phenothiazine in an ester containing a strong acid. It is very common in some commercial processes for product manufacture to occur in the presence of a strong acid and PTZ Phenothiazine is a very effective inhibitor in these cases.

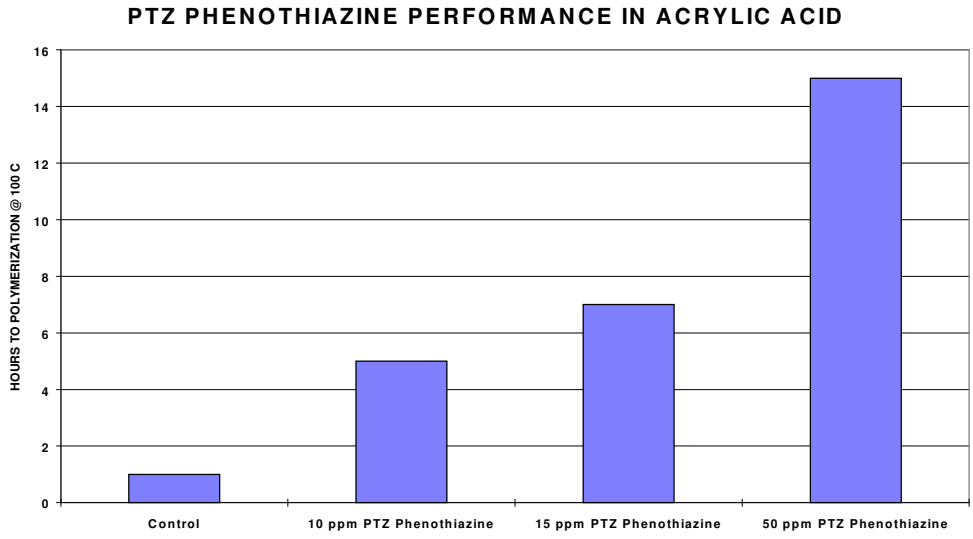
Graph 5



PTZ Performance in Acrylic Acid

Graph 6 details the performance of increasing concentrations of PTZ Phenothiazine in increasing the inherent stability of PTZ Phenothiazine.

Graph 6



Specialty Esters

PTZ Phenothiazine is also utilized in the production of specialty esters that find applications in adhesives, coatings, lubricants and other specialty markets.

3. Shortstopping Applications

In the acrylics industry, it is common practice to utilize PTZ Phenothiazine to shortstop or terminate a runaway acrylic acid or monomer polymerization. Runaway polymerizations can lead to catastrophic events like explosions or fires and it is important that the runaway reaction be terminated as quickly as possible. The addition of up to 1000 ppm of PTZ Phenothiazine will quickly terminate or stop a runaway acrylic acid polymerization. Phenothiazine is the acrylics industry preferred inhibitor for this type of application.

To service the industry, Cytec Industries has developed a series of readily useable PTZ Phenothiazine products that are sold under the Phenothiazine LVT tradename. These products are solutions of PTZ Phenothiazine in various solvents that can be quickly added to runaway polymerizations. These products are described in separate bulletin entitled Liquid Vehicle Technology.

4. Recommended Usage Levels for Acrylic Monomer Stabilization

The following table provides recommendations regarding typical usage levels for PTZ Phenothiazine on a commercial scale in acrylic acid, ester and monomer stabilization.

Applications	PTZ Phenothiazine Use Level (ppm)
In process stabilizer	300 to 1000
Storage/transportation stabilizer	300 to 1000
Shortstopping agent	1000

B. Chloroprene Monomer and Neoprene Polymer

Chloroprene monomer may polymerize during its manufacture, storage and transportation. To prevent this undesirable effect, PTZ Phenothiazine is typically incorporated into chloroprene monomer during its manufacture and storage. During manufacture, the product is utilized at 200 to 1000 ppm during the distillation and purification of the monomer. It may also be added at similar concentrations to protect the monomer during storage and transportation. PTZ Phenothiazine is also used in the production of the neoprene polymer, where it controls polymer molecular weight by functioning as a shortstopping agent.

C. Other Vinyl Monomers

PTZ Phenothiazine also finds application in the stabilization of other monomers and polymers. Other markets for the product include the stabilization of vinyl pyridine, styrene monomer waste streams, vinyl chloride monomer and vinyl acetate. The product is also used in the production of acrylic based polymers. Typical usage levels in these applications range from 100 to 3000 ppm.

D. Polyols For Polyurethanes

The manufacture of polyurethane foams is a highly exothermic process in which a great deal of heat is generated. Additionally, due to the high insulating properties of the foam, it is common for temperatures within the foam to remain high for prolonged periods of time. The exposure of the high surface area of the foam to the oxygen in the air, which enters the foam, and the prolonged high temperatures, create a severe environment for the polyether segment of the polyurethane molecule. Without proper protection, the foam will discolor, may undergo a loss of physical properties and could even begin to burn.

Through the years, the polyurethane industry has developed powerful antioxidant systems to protect the foams against this oxidative attack and the resultant changes in aesthetics, physical properties and potential hazards. Most antioxidant systems in use today in flexible polyurethane foams are comprised of

multicomponent synergistic antioxidant systems. The most common packages are combination of phenolic and amine antioxidants with other additives.

PTZ Phenothiazine is one of the common amine antioxidants that find usage within this industry. Polyurethane foams containing PTZ Phenothiazine exhibit improved scorch resistance and enhanced thermal stability and physical properties. In polyether polyol applications, PTZ Phenothiazine is typically utilized at concentrations ranging from 100 to 500 ppm.

Table 1 demonstrates the lower scorch color and improved physical properties imparted by PTZ Phenothiazine to a flexible polyurethane foam formulation.

Table 1
PTZ Phenothiazine in Polyurethane Foams

Formulation	Scorch Delta E Color	Foam Physical Properties
Control	65	Poor
PTZ Phenothiazine	20	Good

E. Lubricants and Oils

Lubricants and oils are prone to oxidative degradation and the resultant loss of product aesthetics and performance. It is common practice to incorporate synergistic combinations of phenolic and amine antioxidants into lubricants and oils to maintain their product color appearance and quality and functionality in end use applications. Typical lubricants and oils in which PTZ Phenothiazine finds applications include the following:

- Synthetic lubricants and oils
- Functional fluids for the electronic industry
- Heat Transfer Fluid
- Epoxy oils
- Industrial oils
- Engine oils

In these types of oils and lubricants, it is common practice to utilize PTZ Phenothiazine at concentrations ranging from 500 to 5000 ppm.

Table 2 demonstrates the effect of PTZ Phenothiazine in maintaining the color stability of a synthetic lubricant.

Table 2
Color Stability of Synthetic Lubricants

Formulation	Yellowness Index
Control	32.5
PTZ Phenothiazine	27.2

Lubricants were oven aged for 120 days at 50°C

F. Unsaturated Polyesters and Vinyl Esters

PTZ Phenothiazine will function as a product stabilizer, gel retarder and catalyst inhibitor in unsaturated polyester and vinyl ester resins.

Polyester Catalyst Gelation Control

There are times when an effective gelation inhibitor is necessary to prevent premature gelation of catalyzed formulations. This can be during warm weather conditions, or when formulations have been over-catalyzed for a specific application.

Table 3 indicates that PTZ Phenothiazine is extremely effective in retarding gelation rates, using low concentrations. It is significant, that while PTZ phenothiazine affects gel time, it does not deter the polyester from curing once the reaction takes place.

Table 3
PTZ PHENOTHIAZINE'S EFFECT ON GELATION

	1	**2**	**3**	**4**	**5**
Bisphenol-A Polyester	100	100			
Isophthalic Polyester			100	100	100
Cobalt Napthenate	1.0	1.0	0.3	0.3	0.3
Dimethyl Aniline	0.1	0.1	0.1	0.1	0.1
Methyl Ethyl Ketone Peroxide	1.8	1.8	1.5	1.5	1.5
PTZ (10% Solution in MEK)		0.5		0.2	0.5
Room Temperature Curing Times					
Gel Time, Minutes	25	59	6	17	40
Peak Temperature Time, Minutes	9	10	5	7	12
Peak Temp. °C	192	185	205	201	200

Vinyl Ester Product Stabilizer

The product stability of vinyl ester resins is usually not as good as those of polyesters. This is especially true of pre-promoted vinyl ester systems where premature product gelation can sometimes occur within days in warm weather conditions.

Table 4 indicates that the shelf life of promoted vinyl ester systems can be extended appreciably by the addition of PTZ Phenothiazine stabilizer. It also indicates that PTZ Phenothiazine can be added to vinyl esters products at the point of manufacture to insure better product stability.

Table 5 shows that when PTZ Phenothiazine is added to vinyl ester systems utilizing a cumene hydroperoxide cure, it does not affect the gel time appreciably. This is the suggested catalyst for crosslinking vinyl ester resins and PTZ Phenothiazine is the only product that offers both product stability as well as catalyst gelation control in vinyl ester systems.

Table 4
PTZ PHENOTHIAZINE'S EFFECT ON SHELF LIFE

	1	**2**	**3**	**4**
Derekane® 411-45 Resin (Dow Chemical Company)	100	100		
DION VER® 9100 NP Resin (Reichhold Chemicals Inc.)			100	100
Cobalt Napthenate	0.5	0.5	0.5	0.5
PTZ (10% Solution in MEK)		0.5		0.5
Stability at 120°F				
1 Week	Gelled	Good	Good	Good
3 Weeks		Good	Good	Good
4 Weeks		Gelled	Gelled	Good
7 Weeks				Gelled

Table 5
PTZ PHENOTHIAZINE'S EFFECT ON GEL TIME

	1	**2**	**3**
Derekane® 411-45 Resin (Dow Chemical Company)	100	100	100
Dimethyl Aniline	0.1	0.1	0.1
Cobalt Napthenate	0.2	0.2	0.2
PTZ (10% Solution)		0.3	
HQ (10% Solution)			0.5
Cumene Hydroperoxide	1.5	1.5	1.5
Gel Time, Minutes	47	49	>80

G. Pharmaceutical Intermediate

The product may also be used an intermediate in the manufacture of pharmaceutical products.

TECHNICAL SUPPORT INFORMATION

Cytec Industries is committed to providing high quality products and services to our customers. Our marketing/sales, technical, and support organizations operate on a global scale. PTZ Phenothiazine is manufactured at a state of the art, world scale plant located in the USA. We produce product to the highest quality standards and our business is ISO 9002 registered.

Our organization is prepared to provide you with the latest technical and commercial information. We can provide assistance in addressing and resolving product issues, improving processes and developing new innovative technologies. We strive to intimately understand our customers and their markets and to be a world leader in the development of new products and technologies.

SAFETY AND TOXICITY INFORMATION

Cytec Industries has a fully implemented product Stewardship Program and we are prepared to assist our customers by providing the latest safety and handling information on our products. Detailed information on product safety and toxicity is available in the Material Safety Data Sheet for PTZ Phenothiazine. Also, Cytec Industries has extensive experience in the manufacture and safe handling of PTZ Phenothiazine, and we are prepared to share our knowledge. Comprehensive toxicology studies and other relevant safety health and environmental information is also, readily available.

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